3282 © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 3282—3288(1994) [Vol. 67, No. 12

# Generation, ESR Spectra, and Isolation of *N*-(Arylthio)-2,4,6-triarylphenylaminyl Radicals. Influence of the Substituents on the 2,4,6-Triphenyl Groups on the Stabilities of Radicals[1]

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Three *N*-(Arylthio)-2,4,6-tris(4-methylphenyl)-, three *N*-(arylthio)-2,4,6-tris(3-chlorophenyl)-, and five *N*-(arylthio)-2,4,6-tris(4-chlorophenyl)phenylaminyl radicals have been generated by $PbO_2$ oxidation of the corresponding *N*-(arylthio)-2,4,6-triarylanilines and their isolation has been carried out. When electron-donating methyl groups were substituted at the *p*-positions of the 2,4,6-triphenyl groups, the aminyls were less stable, and only one could be isolated as radical crystals. On the other hand, when chloro atoms were substituted at the *m*- or *p*-positions of the 2,4,6-triphenyl groups, the aminyls were more stable and most were isolated. The isolated radical crystals were stable for a long period without any decomposition. The spin density distributions in the radicals are discussed on the basis of the ESR parameters.

Free radicals are inherently transient because they contain an unpaired electron in the highest occupied molecular orbital. However, the electronic stabilization and the steric protection drastically change their stabilities. Typical examples are isolable stable free radicals, such as 2,2-diphenyl-1-picrylhydrazyl, nitroxides, and 1,3,5-triarylverdazyls.[2] Recently, isolable stable free-radical crystals have attracted increasing attention because of the expectation that radical crystals might behave as organic ferromagnets.[3] As part of a program directed toward organic magnetism,[4] we previously studied the generation, ESR spectra, and stabilities of *N*-(arylthio)-2,4,6-triphenylphenylaminyls (**1**) (Chart 1).[5] It has been found that aminyls **1** are quite persistent in solution, even in the presence of oxygen, and can be isolated as radical crystals.[6] This finding prompted us to further study a variety of *N*-(arylthio)-2,4,6-triarylphenylaminyls. In the present study three *N*-(arylthio)-2,4,6-tris(4-methylphenyl)-, three *N*-(arylthio)-2,4,6-tris(3-chlorophenyl)-, and five *N*-(arylthio)-2,4,6-tris(4-chlorophenyl)aminyls (**3**) were generated and their isolation was attempted. In this paper we describe the generation, ESR spectra, and isolation of **3**, as well as the influence of the substituents on the 2,4,6-triphenyl groups on the stabilities of **3**.

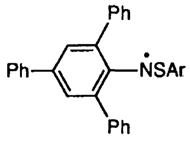

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Chart 1.

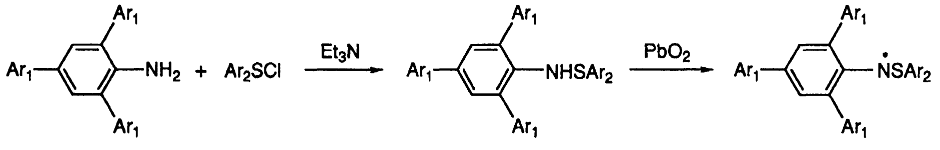
## Results and Discussion

**Preparation of Precursors *N*-(Arylthio)-2,4,6-triarylanilines (2).** *N*-(Arylthio)-2,4,6-tris(4-methylphenyl)- (**2a**—**c**), *N*-(arylthio)-2,4,6-tris(3-chlorophenyl)- (**2d**—**f**), and *N*-(arylthio)-2,4,6-(4-chlorophenyl)anilines (**2g**—**k**) were obtained by a reaction of the corresponding 2,4,6-triarylanilines with arenesulfenyl chlorides in dry ether in the presence of triethylamine (Scheme 1). The 2,4,6-triarylanilines were obtained from the corresponding acetophenones and benzylideneacetophenones, via 2,4,6-triarylpyrylium tetrafluoroborate, according to a literature procedure reported for 2,4,6-triphenylaniline,[7] with some modifications. After column chromatographic separation and subsequent crystallization, pure **2** was obtained in 36—82% yield. Although some of the obtained precursors were colored light green or bluish-green, owing to the contamination with *N*-(arylthio)-2,4,6-triarylphenylaminyl radicals (**3**), this color disappeared upon further recrystallization. The structures were confirmed by the IR and $^1$H NMR spectra and by the elemental analyses.

**Generation and Isolation of 3.** The generation of aminyls **3** was accomplished by oxidation with $PbO_2$. When $PbO_2$ was added to a stirred solution of **2** in benzene, the colorless, light-yellow, or light bluish-green solution immediately turned dark bluish-green (**3a** and **3c**), dark yellowish-green (**3b**), or dark green (**3d**—**k**), and the solution gave an intense ESR signal due to **3**.

As had been expected, aminyls **3** were quite persistent in solution, even in the presence of atmospheric oxygen. This was shown by brief kinetic studies. A benzene solution of **3** (ca. $10^{-4}$ mol dm$^{-3}$) was put in an ESR cell, and the double integrated ESR spectra were recorded at 20 °C for 10 h under atmospheric conditions. Interestingly, no or a negligibly small reduction in the ESR signal intensity was observed during the ESR measurements, indicating that **3** is quite persistent and oxygen-insensitive. Furthermore, even upon cooling to −50 °C, aminyls **3** showed no tendency to dimerize, indicating that they exist solely as the individual radicals. This interesting behavior of **3** prompted us to isolate them.

The isolation procedure was as follows. Precursors **2** were oxidized in benzene with $PbO_2$ in the pres-



2 3

**a**: $Ar_1 = 4\text{-}MeC_6H_4$, $Ar_2 = 3\text{-}NO_2C_6H_4$
**b**: $Ar_1 = 4\text{-}MeC_6H_4$, $Ar_2 = 4\text{-}NO_2C_6H_4$
**c**: $Ar_1 = 4\text{-}MeC_6H_4$, $Ar_2 = 2,4\text{-}Cl_2C_6H_3$
**d**: $Ar_1 = 3\text{-}ClC_6H_4$, $Ar_2 = 3\text{-}NO_2C_6H_4$
**e**: $Ar_1 = 3\text{-}ClC_6H_4$, $Ar_2 = 4\text{-}NO_2C_6H_4$
**f**: $Ar_1 = 3\text{-}ClC_6H_4$, $Ar_2 = 2,4\text{-}Cl_2C_6H_3$
**g**: $Ar_1 = 4\text{-}ClC_6H_4$, $Ar_2 = 4\text{-}ClC_6H_4$
**h**: $Ar_1 = 4\text{-}ClC_6H_4$, $Ar_2 = 3\text{-}NO_2C_6H_4$
**i**: $Ar_1 = 4\text{-}ClC_6H_4$, $Ar_2 = 4\text{-}NO_2C_6H_4$
**j**: $Ar_1 = 4\text{-}ClC_6H_4$, $Ar_2 = 2,4\text{-}Cl_2C_6H_3$
**k**: $Ar_1 = 4\text{-}ClC_6H_4$, $Ar_2 = 3,5\text{-}Cl_2C_6H_3$

Scheme 1.

ence of $K_2CO_3$. After filtration, the solvent was removed by freeze-drying, and a dark-green crystalline residue was twice recrystallized from hexane or hexane–ethyl acetate to give pure radical crystals. The structures of the isolated radicals were confirmed by the IR spectra, showing no NH absorption (in the IR spectra of **2** a strong absorption due to N–H is observed at around 3300 $cm^{-1}$), and by the satisfactory elemental analyses.[8)]

Although *N*-(arylthio)-2,4,6-tris(4-methylphenyl)anilines (**2a**—**c**) were similarly oxidized, aminyl **3b** was only isolated as dark purplish-brown radical crystals in 40% yield. In the case of **2b**, a TLC inspection of the resultant radical solution showed that the oxidation proceeded in high yield with very small amounts of polar byproducts. However, in the case of **2a** and **2c**, considerable amounts of unknown polar byproducts were shown to be formed by a TLC inspection. Furthermore, upon standing of the radical solutions at 0 °C for 2—3 d the aminyl radicals in solution were partly decomposed to give **2a** or **2c** and unknown polar byproducts. The regeneration of **2a** and **2c** can be accounted for in terms of hydrogen-atom abstraction by the aminyls from other coexisting compounds.

Aminyl **3b** was thermally labile. This was recognized in a measurement of the melting point. When the temperature reached ca. 113 °C, dark purplish-brown fine needles were gradually decomposed to give light-brown crystals, which melted at 130—135 °C. Such decomposition was not observed for the other **3** isolated.

The thermal decomposition of **3b** was very complex. A TLC inspection showed the presence of at least six decomposition products. Among them, the main products were **2b** and unknown polar products. Besides them, the formation of a small amount of 2,4,6-tris(4-methylphenyl)aniline was observed as one of the minor products.

On the other hand, *N*-(arylthio)-2,4,6-tris(3-chlorophenyl)- (**3d**—**f**) and *N*-(arylthio)-2,4,6-tris(4-chlorophenyl)phenylaminyls (**3g**—**k**) were more stable, and most were isolated as pure radical crystals in 25—61% yield. The only exception was **3g**, which could not be isolated as radical crystals in spite of much effort, similar to the case of **3a** and **3c**.

All of the radical crystals isolated were stable under ambient conditions and could be stored at 0 °C for a long period without any decomposition. Under acidic conditions, however, they were unstable and rapidly decomposed to give the corresponding 2,4,6-triarylaniline and diaryl disulfide.

**Influence of the Substituents on the Stabilities of 3.** In the present and previous studies,[5)] the isolation of **1** and **3** was carried out. The results are summarized in Table 2. When the X's are H or 3- or 4-Cl and Y is 3- or 4-$NO_2$ or 2,4- or 3,5-$Cl_2$, the corresponding aminyls are sufficiently stable to be isolated as radical crystals, all being isolated as radical crystals. However, when Y was a weaker electron-withdrawing (4-Cl or 4-Br) or electron-donating group (4-Me), the corresponding aminyls were less stable, and isolation was much less easy (X=H, Y=4-Cl or 4-Br) or impossible (**3g**). Thus, their isolation was very often unsuccessful in repeated experimental runs. On the other hand, when the X's were electron-donating methyl groups, the corresponding aminyls were much less stable, and only **3b**, carrying a strong electron-donating 4-$NO_2$ as Y, could be isolated. On the basis of the results it is concluded that, when the X's are H or electron-withdrawing groups and the Y's are also electron-withdrawing groups, the corresponding aminyls can be isolated relatively easily as radical crystals.

Why are the aminyls stabilized by electron-withdrawing substituents? In general, $\rangle$N–S– bonds are much weaker than C–C, C–N, or C–O bonds because there is a repulsion between the nitrogen and sulfur lone pairs of electrons. However, the introduction of electron-withdrawing substituents reduce the lone pair–lone pair repulsion, strengthening the $\rangle$N–S– bonds. Accordingly, when precursors carry an electron-withdrawing substituent(s), oxidation proceeds in high yields, along with the formation very small amounts of polar byproducts. However, if not, oxidation does not proceed satisfactorily, giving considerable amounts of polar byproducts. If they work as hydrogen-donors, the aminyls are additionally consumed by a reaction with the polar byproducts to reproduce the corresponding precursors.

**ESR Parameters.** All of the ESR spectra of **3** are split into a simple 1 : 1 : 1 triplet by an interaction with a nitrogen nucleus, as illustrated in Fig. 1. Although the protons on the *m*-position of the anilino group and on the *o*- and *p*-positions of the phenylthio group are expected to have relatively large hyperfine splitting constants, no hyperfine splittings due to them have been observed, due to a serious line broadening (peak-to-peak linewidth, 0.27—0.30 mT). This line broadening is ascribed to the presence of many unresolved aromatic and methyl protons on the 2,4,6-triaryl groups.

Thioaminyls ($R\dot{N}SR'$) are represented by two major canonical structures (A and B; Scheme 2). This leads to an extensive delocalization of the unpaired electron from the nitrogen atom to the sulfur atom.[9] Since sulfur has a large spin-orbit coupling parameter (382 $cm^{-1}$),[10] this type of conjugative delocalization leads to a considerable increase in the *g* values. The high *g* values of **3** (2.0054—2.0058), compared with typical nitrogen-centered radicals,[11] can therefore be explained by this conjugative delocalization. If the relative importance of A and B is changed by substituents X and Y, the $a_N$ and *g* values should be changed, depending on the electron-donating or electron-withdrawing power of the substituents. As can be seen from Table 1, the $a_N$ and *g* values are almost constant, indicating that the X and Y substituents give no, or a negligibly small, influence on the relative importance of the canonical structures, A and B.

**UV-Visible Spectra.** Aminyls **3** are characterized by the bluish-green (**3a** and **3c**), yellowish-green (**3b**), or green color (**3d**—**k**). Typical UV-visible spectra are shown in Fig. 2, and the UV-visible absorption data for the isolated aminyls are summarized in Table 3. As found in Table 3, aminyls **3** have an absorption peak at around 650 nm, which is ascribed to the green, bluish-green, or yellowish-green color; their large $\varepsilon$ values (7700—9260 $dm^3\,mol^{-1}\,cm^{-1}$) indicate that the absorptions are due to a $\pi$–$\pi^*$ transition. Since ordinal reagents and solvents do not undergo absorptions in such a visible region, the radical concentrations can be readily determined by measuring the visible spectra.

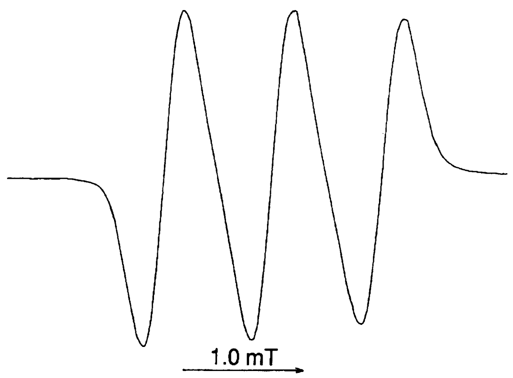
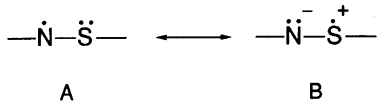


Fig. 1. ESR spectrum of **3a** in benzene at 20 °C.



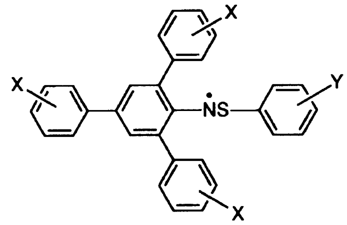
Scheme 2.

Table 1. ESR Parameters for **3** in Benzene at 20 °C

| Radical | $a_N$/mT[a)] | *g* |
|---|---|---|
| **3a** | 0.886 | 2.0054 |
| **3b** | 0.885 | 2.0054 |
| **3c** | 0.894 | 2.0055 |
| **3d** | 0.894 | 2.0055 |
| **3e** | 0.890 | 2.0056 |
| **3f** | 0.887 | 2.0056 |
| **3g** | 0.893 | 2.0058 |
| **3h** | 0.887 | 2.0056 |
| **3i** | 0.887 | 2.0056 |
| **3j** | 0.890 | 2.0057 |
| **3k** | 0.885 | 2.0056 |

a) The value for the central nitrogen.

Table 2. List of the Isolated **1** and **3**[a)]



| | 4-CH3 | 4-Cl | 4-Br | 2,4-Cl2 | 3,5-Cl2 | 3-NO2 | 4-NO2 |
|---|---|---|---|---|---|---|---|
| X=4-CH3 | | | | × | | × | ○ |
| H | × | △ | △ | ○ | ○ | ○ | ○ |
| 3-Cl | | | | ○ | | ○ | ○ |
| 4-Cl | | × | | ○ | ○ | ○ | ○ |

a) ○: Can be easily isolated; △: can be isolated with difficulty; ×: can not be isolated.

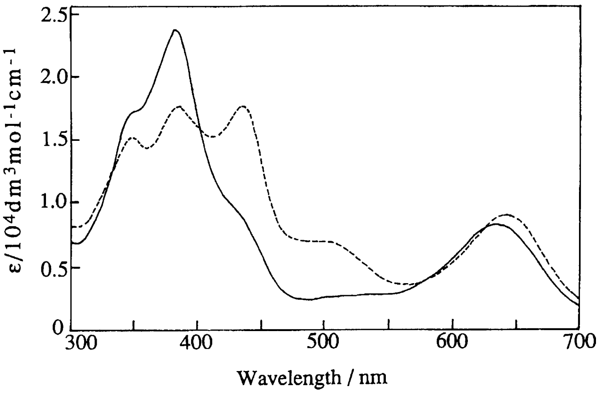


Fig. 2. UV-visible spectra of **3h** (——) and **3i** (- - -) in benzene.

Table 3. UV-Visible Spectral Data of the Isolated **3** in Benzene

| Radical | $\lambda_{\max}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) |
|---|---|
| **3b** | 347 (16200), 386 (18700), 435 (14700), 521 (8190), 640 (9260) |
| **3d** | 343 (15000), 381 (20000), 425 (sh, 10000), 629 (7700) |
| **3e** | 336 (14000), 379 (14800), 431 (17100), 496 (sh, 6890), 636 (8400) |
| **3f** | 340 (sh, 12600), 394 (22300), 447 (sh, 5440), 644 (9080) |
| **3h** | 354 (sh, 17200), 384 (23800), 432 (sh, 9410), 635 (8280) |
| **3i** | 349 (15200), 384 (17700), 434 (17700), 497 (sh, 6920), 642 (9060) |
| **3j** | 350 (sh, 14200), 395 (24300), 450 (sh, 5330), 648 (9150) |
| **3k** | 352 (sh, 15500), 393 (26600), 445 (sh, 5550), 636 (8930) |

Magnetic susceptibility measurements of the isolated radical crystals are in progress.

## Experimental

The melting points were determined on a Yanagimoto micro melting-point apparatus and are uncorrected. The IR spectra were recorded on a JASCO (A-202) spectrometer, and the UV-visible spectra on a Shimadzu (UV 2200) spectrophotometer. The $^1$H NMR spectra were measured with a JEOL (GX-400) spectrometer (400 MHz). The chemical shifts are expressed in ppm values ($\delta$) using TMS as an internal standard. The ESR spectra were recorded on a JEOL (JES-ME-3X) or Bruker (ESP 300) spectrometer equipped with an X-band microwave unit and 100 KHz field modulation. The hyperfine splitting constants and $g$ values were determined by simultaneous measurements with Fremy's salt in an aqueous $K_2CO_3$ solution used as a reference ($a_N$=1.309 mT; $g$=2.0057).

**Materials.** Dry diethyl ether (ether) was obtained by distillation from sodium benzophenone. Anhydrous methanol was obtained by distillation from $(MeO)_2Mg$. Triethylamine and anhydrous ethanol were commercial grade. 4-Chloro-, 4-bromo-, 2,4-dichloro-, 3,5-dichloro-, 4-nitro-, and 3-nitrobenzenesulfenyl chlorides were prepared by previously reported procedures.[5,12]

2,4,6-Tris(4-methylphenyl)-, 2,4,6-tris(3-chlorophenyl)-, and 2,4,6-tris(4-chlorophenyl)anilines were prepared from the corresponding benzylideneacetophenones and acetophenones according to the procedure reported for 2,4,6-triphenylaniline,[7] with some modifications.

**2,4,6-Tris(4-methylphenyl)pyrylium Tetrafluoroborate:** A solution of 43.7 g (0.186 mol) of 4′-methyl-2-(4-methylbenzylidene)acetophenone, 12.5 g (0.093 mol) of 4′-methylacetophenone in 65 cm$^3$ of 1,2-dichloroethane was warmed to 70—75 °C with stirring. After a 52% ethereal solution (30 cm$^3$) of tetrafluoroboric acid was added dropwize during 30 min, the resulting red–orange mixture was heated under reflux for 1 h with stirring, and cooled at 0 °C overnight. A deposited yellow powder product was filtered, washed well with ether, and dried. Yield 61% (25.0 g, 0.0570 mol).

**2,4,6-Tris(4-methylphenyl)-1-nitrobenzene:** To a suspension of 27.0 g (0.0616 mol) of 2,4,6-tris(4-methylphenyl)pyrylium tetrafluoroborate, 4.3 cm$^3$ of nitromethane in 72 cm$^3$ of anhydrous ethanol was added 14.4 cm$^3$ of triethylamine at once. After the mixture was heated under reflux for 3 h with stirring, the resulting homogeneous reaction mixture was cooled at 0 °C overnight. Deposited slightly brownish fine plates were filtered, washed well with cold methanol, and dried. Yield 66% (16.0 g, 0.0407 mol); mp 160—162 °C (lit,[13] 157—158 °C).

**2,4,6-Tris(4-methylphenyl)aniline:** A mixture of 12.0 g (0.0305 mol) of 2,4,6-tris(4-methylphenyl)-1-nitrobenzene in 460 cm$^3$ of anhydrous methanol was heated under reflux over 678 g of 4 wt% sodium amalgam. After 2 d, both the hot methanol solution and the deposited crystals were poured into a large amount of ice-water. Slightly yellowish fine prisms were collected by filtration, washed well with water, and dried. Yield 93% (10.4 g, 0.0285 mol); mp 113—115 °C (lit,[13] 113—114 °C); IR (KBr) 3440 and 3350 cm$^{-1}$ ($NH_2$); $^1$H NMR ($CDCl_3$) $\delta$=2.36 (s, $CH_3$, 3H), 2.41 (s, $CH_3$, 6H), ca. 3.75 (br. s, $NH_2$, 2H), and 7.24—7.48 (m, aromatic, 14H).

**2,4,6-Tris(3-chlorophenyl)pyrylium Tetrafluoroborate:** A solution of 68.0 g (0.0246 mol) of 3′-chloro-2-(3-chlorobenzylidene)acetophenone, 19.0 g (0.123 mol) of 3′-chloroacetophenone in 86 cm$^3$ of 1,2-dichloroethane was warmed to 70—75 °C with stirring. After a 52% ethereal solution (42 cm$^3$) of tetrafluoroboric acid was added during 30 min with stirring, the resulting red–orange mixture was heated under reflux for 1 h with stirring and cooled at 0 °C overnight. A deposited yellow powder product was filtered, washed well with ether, and dried. Yield 51% (31.6 g, 0.0632 mol).

**2,4,6-Tris(3-chlorophenyl)-1-nitrobenzene:** To a stirred suspension of 31.0 g (0.0621 mol) of 2,4,6-tris(3-chlorophenyl)pyrylium tetrafluoroborate and 5.5 cm$^3$ of nitromethane in 91 cm$^3$ of anhydrous ethanol was added 18.2 cm$^3$ of triethylamine. After the mixture was heated under reflux for 3 h with stirring, the resulting homogeneous solution was cooled at 0 °C overnight. Deposited slightly brownish fine prisms were filtered, washed well with cold methanol, and dried. Yield 55% (15.5 g, 0.0341 mol); mp 176—178 °C.

**2,4,6-Tris(3-chlorophenyl)aniline:** A mixture of 11.3 g (0.0247 mol) of 2,4,6-tris(3-chlorophenyl)-1-nitrobenzene in 450 cm$^3$ of anhydrous methanol was heated under reflux over 521 g of 4 wt% sodium amalgam. After 1 d, both the hot methanol solution and the deposited crystals were poured into a large amount of ice-water. The deposited slightly brownish fine needles were collected with filtration, washed well with water, and dried. Yield 96% (10.1 g, 0.0238 mol); mp 86—88 °C; IR (KBr) 3420 and 3360 cm$^{-1}$ ($NH_2$); $^1$H NMR ($CDCl_3$) $\delta$=3.91 (br. s, $NH_2$, 2H) and 7.23—7.55 (m, aromatic, 14H).

**2,4,6-Tris(4-chlorophenyl)pyrylium Tetrafluoroborate:** A solution of 45.4 g (0.164 mol) of 4′-chloro-2-(4-chlorobenzylidene)acetophenone, 12.7 g (0.082 mol) of 4′-chloroacetophenone in 167 cm$^3$ of 1,2-dichloroethane was warmed to 70—75 °C with stirring. After a 52% ethereal solution (27 cm$^3$) of tetrafluoroboric acid was added dropwize during 30 min with stirring, the resulting red–orange mixture was heated under reflux for 1 h with stirring and cooled at 0 °C overnight. A deposited yellow powder product was filtered, washed well with ether, and dried. Yield 60% (24.8 g, 0.0496 mol).

**2,4,6-Tris(4-chlorophenyl)-1-nitrobenzene:** To a suspension of 24.4 g (0.0488 mol) of 2,4,6-tris(4-chlorophenyl)pyrylium tetrafluoroborate, 3.9 $cm^3$ of nitromethane in 57 $cm^3$ of anhydrous ethanol was added 11.4 $cm^3$ of triethylamine. After the mixture was heated under reflux for 3 h with stirring, the resulting homogeneous mixture was cooled at 0 °C overnight. Deposited slightly brownish fine prisms were filtered, washed well with cold methanol, and dried. Yield 77% (17.0 g, 0.0374 mol); mp 209—211 °C.

**2,4,6-Tris(4-chlorophenyl)aniline:** A mixture of 12.0 g (0.0264 mol) of 2,4,6-tris(4-chlorophenyl)-1-nitrobenzene in 500 $cm^3$ of anhydrous methanol was heated under reflux over 586 g of 4 wt% sodium amalgam. After 3 d, both the hot methanol solution and the deposited crystals were poured into a large amount of ice-water. The deposited colorless fine needles were collected with filtration, washed well with water, and dried. Yield 87% (9.77 g, 0.0230 mol); mp 154—155 °C; IR (KBr) 3420 and 3380 $cm^{-1}$ ($NH_2$); $^1H$ NMR ($CDCl_3$) $\delta$=3.80 (br. s, $NH_2$, 2H) and 7.30—7.48 (m, aromatic, 14H).

**General Procedure for the Preparation of *N*-(Arylthio)-2,4,6-triarylaniline (2).** To a stirred solution of 4.13 mmol of a 2,4,6-triarylaniline and 10.8 mmol (1.09 g) of triethylamine in 100—200 $cm^3$ of dry ether was added dropwise a solution of 6.2 mmol of arenesulfenyl chloride in 30 $cm^3$ of dry ether at 0 °C. After the addition was completed, the mixture was stirred for 2 h at the same temperature and filtered. The filtrate was evaporated under reduced pressure, and the residue was column chromatographed on alumina (Merck, aluminium oxide 90, column size 4×20 cm) using 1:4 (**2f**, **2g**, **2k**), 1:3 (**2c**, **2j**), 1:1 (**2a**, **2b**, **2d**), or 2:1 (**2e**, **2h**, **2i**) benzene–hexane as an eluant. Crystallization from an appropriate solvent gave pure crystals of **2**.

***N*-(3-Nitrophenylthio)-2,4,6-tris(4-methylphenyl)aniline (2a):** Light green fine prisms (from ethanol); mp 70—72 °C; yield 45%; IR (KBr) 3330 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=2.27 (s, $CH_3$, 3H), 2.29 (s, $CH_3$, 6H), 5.40 (s, NH, 1H), and 7.07—7.83 (m, aromatic, 18H). Found: C, 77.02; H, 5.68; N, 5.09%. Calcd for $C_{33}H_{28}N_2O_2S$: C, 76.71; H, 5.46; N, 5.42%.

***N*-(4-Nitrophenylthio)-2,4,6-tris(4-methylphenyl)aniline (2b):** Yellow fine plates (from ethanol–benzene); mp 136—138 °C; yield 82%; IR (KBr) 3300 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=2.31 (s, $CH_3$, 6H), 2.71 (s, $CH_3$, 3H), 5.36 (s, NH, 1H), 6.89 (d, $J$=9.2 Hz, *o*- or *m*-H of the arylthio group, 2H), 7.12—7.49 (m, aromatic, 14H), 7.87 (d, $J$=9.2 Hz, *o*- or *m*-H of the arylthio group, 2H). Found: C, 77.06; H, 5.52; N, 5.16%. Calcd for $C_{33}H_{28}N_2O_2S$: C, 76.71; H, 5.46; N, 5.42%.

***N*-(2,4-Dichlorophenylthio)-2,4,6-tris(4-methylphenyl)aniline (2c):** Colorless fine needles (from ethanol– benzene); mp 174—176 °C; yield 44%; IR (KBr) 3300 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=2.33 (s, $CH_3$, 6H), 2.36 (s, $CH_3$, 3H), 5.20 (s, NH, 1H), and 6.88–7.49 (m, aromatic, 17H). Found: C, 73.05: H, 4.88; N, 2.37%. Calcd for $C_{33}H_{27}Cl_2NS$: C, 73.32; H, 5.04; N, 2.59%.

***N*-(3-Nitrophenylthio)-2,4,6-tris(3-chlorophenyl)aniline (2d):** Light yellow fine prisms (from ethanol); mp 125—127 °C; yield 54%; IR (KBr) 3310 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.30 (s, NH, 1H) and 7.08—7.90 (m, aromatic, 18H). Found: C, 62.55; H, 3.41; N, 4.57%. Calcd for $C_{30}H_{19}Cl_3N_2O_2S$: C, 62.35; H, 3.31; N, 4.85%.

***N*-(4-Nitrophenylthio)-2,4,6-tris(3-chlorophenyl)aniline (2e):** Yellow fine prisms (from ethanol); mp 81—84 °C; yield 54%; IR (KBr) 3310 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.26 (s, NH, 1H), 6.95 (d, $J$=8.5 Hz, *o*- or *m*-H of the arylthio group, 2H), 7.20—7.56 (m, aromatic, 14H), and 7.96 (d, $J$=8.5 Hz, *o*- or *m*-H of the arylthio group, 2H). Found: C, 62.46; H, 3.49; N, 4.64%. Calcd for $C_{30}H_{19}Cl_3N_2O_2S$: C, 62.35; H, 3.31; N, 4.85%.

***N*-(2,4-Dichlorophenylthio)-2,4,6-tris(3-chlorophenyl)aniline (2f):** Light brown fine prisms (from ethanol); mp 124—126 °C; yield 56%; IR (KBr) 3320 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.17 (s, NH, 1H) and 6.94—7.56 (m, aromatic, 17H). Found: C, 60.20; H, 3.10; N, 2.26%. Calcd for $C_{30}H_{18}Cl_5NS$: C, 59.87; H, 3.01; N, 2.33%.

***N*-(4-Chlorophenylthio)-2,4,6-tris(4-chlorophenyl)aniline (2g):** Colorless fine needles (from ethanol and then hexane); mp 145—146 °C; yield 36%; IR (KBr) 3350 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.24 (s, NH, 1H) and 6.73—7.50 (m, aromatic, 18H). Found: C, 63.40; H, 3.21; N, 2.25%. Calcd for $C_{30}H_{19}Cl_4NS$: C, 63.51; H, 3.38; N, 2.47%.

***N*-(3-Nitrophenylthio)-2,4,6-tris(4-chlorophenyl)aniline (2h):** Yellow fine prisms (from ethanol–benzene); mp 113—114 °C; yield 80%; IR (KBr) 3300 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.30 (s, NH, 1H) and 7.08—7.92 (m, aromatic, 18H). Found: C, 62.30; H, 3.41; N, 4.49%. Calcd for $C_{30}H_{19}Cl_3N_2O_2S$: C, 62.35; H, 3.31; N, 4.85%.

***N*-(4-Nitrophenylthio)-2,4,6-tris(4-chlorophenyl)aniline (2i):** Yellow plates (from ethanol–benzene); mp 176—177 °C; yield 65%; IR (KBr) 3310 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.25 (s, NH, 1H), 6.91 (d, $J$=8.5 Hz, *o*- or *m*-H of the arylthio group, 2H), 7.25—7.50 (m, aromatic, 14H), and 7.95 (d, $J$=8.5 Hz, *o*- or *m*-H of the arylthio group, 2H). Found: C, 62.08; H, 3.16; N, 4.59%. Calcd for $C_{30}H_{19}Cl_3N_2O_2S$: C, 62.35; H, 3.31; N, 4.85%.

***N*-(2,4-Dichlorophenylthio)-2,4,6-tris(4-chlorophenyl)aniline (2j):** Colorless fine needles (from ethanol–benzene); mp 171—173 °C; yield 60%; IR (KBr) 3320 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.12 (s, NH, 1H) and 6.88—7.50 (m, aromatic, 17H). Found: C, 60.13; H, 2.90; N, 2.15%. Calcd for $C_{30}H_{18}Cl_5NS$: C, 59.87; H, 3.01; N, 2.33%.

***N*-(3,5-Dichlorophenylthio)-2,4,6-tris(4-chlorophenyl)aniline (2k):** Colorless plates (from ethanol); mp 143—145 °C; yield 41%; IR (KBr) 3300 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$=5.22 (s, NH, 1H) and 6.65—7.50 (m, aromatic, 17H). Found: C, 59.88; H, 3.02; N, 2.32%. Calcd for $C_{30}H_{18}Cl_5NS$: C, 59.87; H, 3.01; N, 2.33%.

**Oxidation of 2 to *N*-(Arylthio)-2,4,6-triarylphenylaminyls (3).** Compound **2** (200 mg) was dissolved in 20 $cm^3$ of benzene with stirring. After 2.0 g of $K_2CO_3$ was added, 2.0 g of $PbO_2$[14)] was added in some portions during 2 min with stirring; the resulting colored mixture was stirred further for 0.5 min. After filtration, the solvent was removed by freeze-drying. The crystalline residue was twice recrystallized from an appropriate solvent.

***N*-(4-Nitrophenylthio)-2,4,6-tris(4-methylphenyl)-phenylaminyl (3b):** Dark-purplish brown fine needles (from hexane); mp 130—135 °C (decompose at around 113 °C to give light brown crystals); yield 40%; IR (KBr) 2900, 1565, 1510, 1330, 850, 815, and 740 cm$^{-1}$. Found: C, 77.06; H, 5.52; N, 5.16%. Calcd for $C_{33}H_{27}N_2O_2S$: C, 76.86; H, 5.28; N, 5.43%.

***N*-(3-Nitrophenylthio)-2,4,6-tris(3-chlorophenyl)-phenylaminyl (3d):** Dark-blue fine needles (from hexane–ethyl acetate); mp 113—115 °C; yield 45%; IR (KBr) 1585, 1560, 1525, 1470, 1345, 1200, 1100, 1080, 870, 780, 740, 730, and 700 cm$^{-1}$. Found: C, 62.18; H, 3.10; N, 4.65%. Calcd for $C_{30}H_{18}Cl_3N_2O_2S$: C, 62.46; H, 3.14; N, 4.86%.

***N*-(4-Nitrophenylthio)-2,4,6-tris(3-chlorophenyl)-phenylaminyl (3e):** Dark-blue fine prisms (from hexane–ethyl acetate); mp 117—119 °C; yield 49%; IR (KBr) 1590, 1570, 1515, 1470, 1335, 1080, 855, 790, 720, and 700 cm$^{-1}$. Found: C, 62.29; H, 3.39; N, 4.70%. Calcd for $C_{30}H_{18}Cl_3N_2O_2S$: C, 62.46; H, 3.14; N, 4.86%.

***N*-(2,4-Dichlorophenylthio)-2,4,6-tris(3-chlorophenyl)phenylaminyl (3f):** Dark-green fine needles (from hexane); mp 120—121 °C; yield 48%; IR (KBr) 1580, 1560, 1470, 1440, 1215, 1090, 1030, 870, 780, and 690 cm$^{-1}$. Found: C, 60.16; H, 2.98; N, 2.11%. Calcd for $C_{30}H_{17}Cl_5NS$: C, 59.97; H, 2.85; N, 2.33%.

***N*-(3-Nitrophenylthio)-2,4,6-tris(4-chlorophenyl)-phenylaminyl (3h):** Dark-green fine needles (from hexane–ethyl acetate); mp 147—149 °C; yield 37%; IR (KBr) 1565, 1520, 1480, 1345, 1090, 1010, 820, and 730 cm$^{-1}$. Found: C, 62.35; H, 3.15; N, 5.20%. Calcd for $C_{30}H_{18}Cl_3N_2O_2S$: C, 62.46; H, 3.14; N, 4.86%.

***N*-(4-Nitrophenylthio)-2,4,6-tris(4-chlorophenyl)-phenylaminyl (3i):** Dark-purplish brown fine needles (from hexane–ethyl acetate); mp 132–134 °C; yield 61%; IR (KBr) 1585, 1570, 1510, 1480, 1340, 1090, 1010, 850, 820, and 740 cm$^{-1}$. Found: C, 62.78; H, 3.45; N, 4.65%. Calcd for $C_{30}H_{18}Cl_3N_2O_2S$: C, 62.46; H, 3.14; N, 4.86%.

***N*-(2,4-Dichlorophenylthio)-2,4,6-tris(4-chlorophenyl)phenylaminyl (3j):** Dark-green fine needles (from hexane–ethyl acetate); mp 122—124 °C; yield 35%; IR (KBr) 1580, 1560, 1540, 1480, 1440, 1370, 1090, 1030, 1010, 870, and 815 cm$^{-1}$. Found: C, 60.24; H, 3.09; N, 2.04%. Calcd for $C_{30}H_{17}Cl_5NS$: C, 59.97; H, 2.85; N, 2.33%.

***N*-(3,5-Dichlorophenylthio)-2,4,6-tris(4-chlorophenyl)phenylaminyl (3k):** Dark-green fine needles (from hexane–ethyl acetate); mp 175—178 °C; yield 25%; IR (KBr) 1580, 1560, 1480, 1410, 1400, 1380, 1220, 1135, 1090, 1015, 845, 830, 820, 800, and 660 cm$^{-1}$. Found: C, 60.08; H, 2.91; N, 2.51%. Calcd for $C_{30}H_{17}Cl_5NS$: C, 59.97; H, 2.85; N, 2.33%.

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9) In a previous study$^{5)}$ satellite lines due to $^{33}S$ at natural abundance were detected in the ESR spectra of *N*-(4-bromophenylthio)- and *N*-[(4-bromophenyl-$d_4$)thio]-2,4,6-tri(phenyl-$d_5$)phenylaminyls, and the $a_{^{33}\mathrm{S}}$ values were determined to be 0.462—0.51 mT. If McConnell's relation ($a_\mathrm{x}=Q_\mathrm{x}\rho_\mathrm{x}^\pi$) is applied, the $\rho_\mathrm{S}^\pi$ values can be estimated from the $a_{^{33}\mathrm{S}}$ values to be 0.20—0.22 (as the $Q_{^{33}\mathrm{S}}$ constant, 2.3 mT is employed): Y. Miura, H. Asada, M. Kinoshita, and K. Ohta, *J. Phys. Chem.*, **87**, 3450 (1983).

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oxidation conditions. Since **2** and **3** are rapidly decomposed under acidic conditions, commercially available $PbO_2$ (purchased from Hayashi Pure Chemical Company, Inc.) was treated with 2 M NaOH under reflux for 2 h, washed with water, and dried completely over $P_2O_5$ in vacuo, prior to use ($M = mol\,dm^{-3}$).